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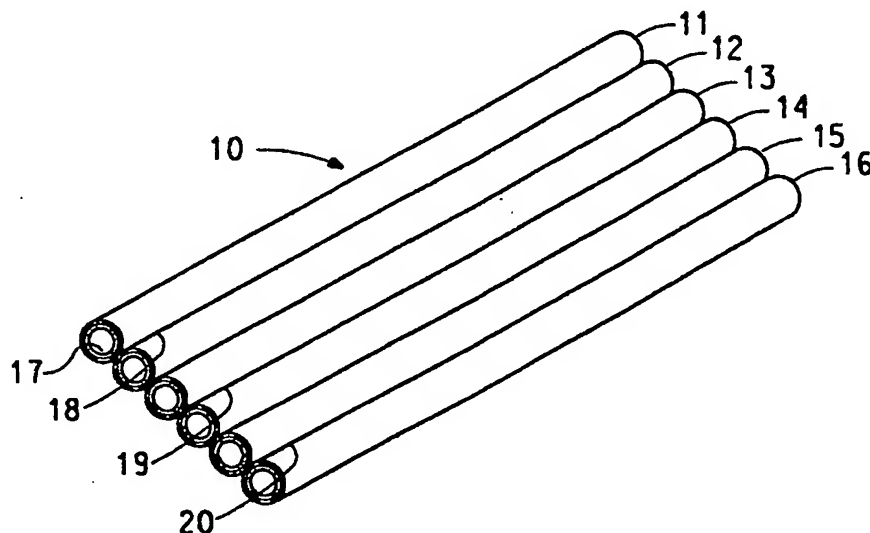
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(54) Title: HEAT EXCHANGER FORMED FROM TUBES JOINED BY THERMAL BONDING



(57) Abstract: Heat exchangers are made of polymeric tubes (11-16) joint together. The outer surface of the tubes (11-16) is made of a lower melting polymer to thermally bond adjacent tubes (11-16) together to form a tube sheet (10).

WO 00/79199 A1

TITLEHEAT EXCHANGER FORMED FROM TUBES JOINED BY THERMAL
BONDINGBACKGROUND OF THE INVENTION

5 Efficient plate type units (panels) used in nylon heat exchangers are produced by a twin sheet thermoforming process with internal gas assist, which gives an essentially flat plate consisting of a number of tubes joined by ligatures formed from the sheets of nylon. This process is described in US 5,195,240.

10 Such plates and the heat exchangers formed from them provide excellent heat transfer efficiency for the space volume occupied, but can tolerate only relatively low internal pressures, restricting their applicability. Tubing formed by extrusion can tolerate much higher internal pressure. In a high efficiency
15 exchanger a large number of small tubes are required; constraint and support of these tubes is required. Use of tubing located between two bonded sheets of plastic to achieve this support is described in US 5,469,915. However, this still requires ligatures between the tubes, which reduces heat transfer efficiency.

20 Patents and applications on prior attempts in this area include: US 5,195,240 "Method for the Manufacture of Thermoplastic Panel Heat Exchanger", J.P.Shuster and A.J.Cesaroni, Apr.16,1992, assigned to DuPont Canada Inc.; US 5,469,915 "Panel Heat Exchanger formed from Tubes and Sheet", A.J.Cesaroni, Nov. 28,1995; US Patent Application No. 60/014,150 filed March 25,1997,
25 N.A.Farkas; and U. S. Application Ser. No. 09/089,888, filed June 6, 1997 "Solventless Panel Forming Process", S.R.Doshi, N.A.Farkas and K.E.Stevens

SUMMARY OF THE INVENTION

30 The present invention provides A heat exchanger made from polymeric tubes in the form of tube sheets with a multiplicity of at least three tubes adjacent each other in a plane, bonded together by an outer layer on the tubes which is melted together.

BRIEF DESCRIPTION OF THE DRAWINGS

35 Fig. 1 is a schematic representation of a tube sheet of the invention, prior to melt bonding.

Fig. 2 is a schematic view of a tube of the invention with outer and inner layers.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

5 We have developed alternate panels constructed from tubes and processes to construct these panels, wherein the tubes are bonded to each other in a parallel, essentially flat manner with no ligature between the tubes. The outer (surface) layer of the tube is a polyamide modified to be thermally bondable, eliminating the need for phenol. These tubes can be produced by coextrusion of a thin layer
10 of nylon 6/30% D12/ 24% Surlyn 9320/ 12% EBAGMA 4934-1/ 2.5% Irganox 1010/1098/ 0.75% Zinc stearate, or equivalently, Zytel FN 726/ 30% D12, on to a main structural layer of nylon 6,6 or modified nylon 6,6. Additional layers of thermoplastic can be incorporated into the tubing by coextrusion to enhance other properties, such as incorporating a layer of thermotropic liquid crystal polymer
15 (LCP) to enhance the moisture barrier of the structure.

Panel formation from these tubes is accomplished by heating a bundle of tubes constrained in intimate contact in a parallel, essentially flat manner such that bonding between the tubes occurs. This can be accomplished for example, by
20 heating with hot air or an oven, such that the surface temperature of the tubes reaches about 200°C to effect tube to tube bonding.

Fig. 1 shows tubes 11 – 16 of the invention laid adjacent to each other to form a tube sheet 10, with interstices at 18 – 20 and with holes 17 in the tubes.
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Fig. 2 shows an enlarged view of a tube 11 used in the invention, with an outer layer 21, an inner layer 22 and a hole 17.

The tubes can be made from a variety of materials, including a polyamide
30 modified to be thermally bondable or heat-sealable, eliminating the need for phenol. These films can be produced by coextrusion of a thin bondable layer (0.013-0.076 mm) preferably of a blend of polycaprolactam (19-40% by weight) polymer prepared from equimolar amounts of 2-methylpentamethylene diamine and 1,12-dodecanedioic acid (20-40% by weight) such as "D-12" high
35 performance nylon sold by DuPont, a copolymer of ethylene and a vinyl carboxylic acid, partially neutralized by a Group 1A,2A or 3A metal ion (15-58% by weight) such as "Surlyn" ionomer sold by DuPont, and a polymeric grafting agent (3-16% by weight) such as "EBAGMA" grafting agent sold by DuPont,

optionally containing heat stabilizers, pigments and other known adjuvants, onto a main structural layer (2-10 mil) of polyamide film. Formulations for the bondable inner layer are further described in US Patent Application No. 60/014,150, filed March 25, 1996, incorporated herein by reference. Panel formation can be carried out with the same equipment, under minor modifications to the process.

The polyamide-based composition of the inner layer of each sheet is a heat formable laminating film made from a multi-phase thermoplastic resin composition comprising the following main components:

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- i) at least one polyamide resin selected from aliphatic and semi-aromatic polyamides that can be either semi-crystalline or amorphous in structure having a number average molecular weight of at least about 5000;
 - 15 ii) at least one polyamide resin comprising at least one pendant alkyl branch having 1 to 3 carbon atoms within at least two amide linkages along the polymer backbone and at least one sequence of at least seven consecutive carbon atoms, excluding carbon atoms in pendant alkyl branches, if any, within at least two amide linkages along the polymer backbone, the melting
20 point of the polyamide being less than 200°C;
- the polyamides of i) and ii) having graft sites and forming the continuous phase of the composition;
- 25 iii) at least one ethylene copolymer, E/X/Y, where E is ethylene and is at least 50 % by weight of E/X/Y, X is from 1-35 % by weight of an acid containing unsaturated mono-carboxylic acid, and Y is 0-49 % by weight of a moiety derived from at least one alkyl acrylate, alkyl methacrylate, alkyl vinyl ether, carbon monoxide, sulfur dioxide, or mixtures thereof where the alkyl groups
30 contain 1-12 carbon atoms, and further wherein the acid groups in the acid-containing moiety are neutralized from 0-100% by weight of a metal ion;
 - 35 iv) at least one polymeric grafting agent which contains reactive groups selected from at least one of epoxides, isocyanates, aziridines, silanes, alkyl halides, alpha-halo ketones and aldehydes, or oxazoline, which reacts with the acid-containing moieties in component iii) and additionally reacts with the graft sites of components i) and ii), and the weight percent of the monomer(s) containing the reactive groups is 0.5-15 weight percent of the polymeric

grafting agent, and the remainder of the polymeric grafting agent contains at least 50 % by weight of ethylene and from 0-49 % by weight of a moiety derived from at least one alkyl acrylate, alkyl methacrylate, alkyl vinyl ether, carbon monoxide, sulfur dioxide, or mixtures thereof where the alkyl groups contain 1-12 carbon atoms.

The components are combined as follows:

from about 17 to about 54% by weight of component i), from about 1 to about 40% by weight of component ii), from about 5 to about 69% by weight of component iii), and from about 0.5 to about 45% by weight of component iv); such that the sum of components i) and ii) equals from about 29 to about 72% by weight.

In another embodiment of the invention there is provided a novel multi-phase resin composition comprising as the main components:

from about 17 to about 54% by weight of (i) at least one polyamide resin selected from aliphatic and semi-aromatic polyamides that can be either semi-crystalline or amorphous in structure having a number average molecular weight of at least about 5000, wherein the semi-crystalline polyamides have a melting point greater than 200°C.

Polymers that may be used in the tubes include nylon 66, nylon 6, blends of nylon 6 and nylon 66, and other materials, including: from about 1 to about 40 % by weight of (ii) at least one polyamide resin comprising at least one pendant alkyl branch having 1 to 3 carbon atoms within at least two amide linkages along the polymer backbone and at least one sequence of at least seven consecutive carbon atoms, excluding carbon atoms in pendant alkyl branches, if any, within at least two amide linkages along the polymer backbone, the melting point of the polyamide being less than 200°C; the polyamides of i) and ii) having graft sites and forming the continuous phase of the composition; and with the proviso that the sum of components i) and ii) is from about 29 to about 72% by weight;

from about 5 to about 69% by weight of (iii) at least one ethylene copolymer, E/X/Y, where E is ethylene and is at least 50 % by weight of E/X/Y, X is from 1-35 % by weight of an unsaturated mono-carboxylic acid, and Y is 0-49 % by weight of a moiety derived from at least one alkyl acrylate, alkyl

methacrylate, alkyl vinyl ether, carbon monoxide, sulfur dioxide, or mixtures thereof where the alkyl groups contain 1-12 carbon atoms, and further wherein the acid groups in the acid-containing moiety are neutralized from 0-100% by weight of a metal ion; and

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from about 0.5 to 45% by weight of (iv) at least one polymeric grafting agent which contains reactive groups selected from at least one of epoxides, isocyanates, aziridines, silanes, alkyl halides, alpha-halo ketones and aldehydes, or oxazoline, which grafting agents react with the acid-containing moieties in component iii) and additionally react with the graft sites of components i) and ii), and the weight percent of the monomer(s) containing the reactive groups is 0.5-15 weight percent of the polymeric grafting agent, and the remainder of the polymeric grafting agent contains at least 50 % by weight of ethylene and from 0-49 % by weight of a moiety derived from at least one alkyl acrylate, alkyl methacrylate, alkyl vinyl ether, carbon monoxide, sulfur dioxide, or mixtures thereof where the alkyl groups contain 1-12 carbon atoms.

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In a preferred form of the invention, the end group balance of the low temperature nylon has been found to affect the processing and properties of the final film product. In other words, it has been found that high performance nylon, specifically D12, with balanced or carboxyl rich end groups in the formulation reduces filter pressure drops and melt viscosities during film production, and improves film dimensional stability during heating - compared to the incorporation of D12 having amine-rich ends.

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A preferred form of the present formulation comprises from about 17 to about 54% by weight, more preferably, from about 18 to about 47% by weight, and most preferably, from about 19 to about 40% by weight of Nylon 6 (component i); from about 1 to about 40% by weight, more preferably about 10 to about 40% by weight; most preferably from about 20 to about 40% by weight of Nylon D12 (low temperature nylon), (component ii); from about 5 to about 69%, more preferably from about 11 to about 58% by weight, and most preferably from about 15 to about 48% by weight of ethylene E/X/Y (component iii); from about 0.5 to about 45% by weight, more preferably from about 2 to about 28%, most preferably from about 3 to about 16% by weight of EBAGMA (component iv); with the total amount of nylon ranging preferably from about 29 to about 72% by weight, more preferably from about 38 to about 71% by weight, and most preferably from about 45 to about 70% by weight.

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It should be noted that for the ranges set out above these may be applied to the various generic components also.

5 In another preferred form of the invention, the formulation comprises from about 55 to about 80% by weight of components (i) and (ii), with the nylon components I) and ii) taken together always in the majority (the iii) component which can be "SURLYN" ionomer produced by DuPont, and the iv) coponent which can be "EBAGMA" comaptibilizer produced by DuPont, are in the
10 minority), but component (i) may range from about 20 to about 60% by weight, and component (ii) may range from about 10 to about 35% by weight.

In every instance, the formulations disclosed herein may include antioxidants, heat stabilizers or mixtures thereof. Typically these comprise from
15 about 0.05 to about 5.0% by weight, preferably from about 0.05 to about 2.0% by weight. Organic heat stabilizers have been found to be better than the metal halide heat stabilizers, such as CuI/KI, in terms of retention of film physical properties after oven aging for one hour at 200°C. "Irganox" 1010/1098 blend of two hindered phenolic antioxidants produced by Ciba Specialty Chemicals is a
20 preferred example of such a material. This substance also reduces filter pluggage and reduces pressure during the production of the film.

Other optional ingredients may be selected from flame retardants, anti-blocking agents, slip additives, pigments or dyes, processing aids, plasticizers and
25 ultra-violet blocking agents. These may be used in suitable quantities as are well known to those skilled in the art.

Liquid crystal polymers can also be used in forming layers in the tubes, including: One of the materials which is part of the HESM is an isotropic thermoplastic (ITP). Isotropic herein means that the polymer is isotropic when
30 tested by the TOT Test described in U.S. Patent 4,118,372, which is hereby included by reference. Any ITP may be used so long as it meets certain requirements. It must of course withstand the temperatures to which the HESM is exposed, and should throughout that temperature range provide sufficient strength
35 (together with the LCP) to the HESM to reasonably maintain its shape and contain the fluids in the heat exchanger, as needed. If it is exposed to one or more of the fluids in the heat exchanger (or any other adventitious materials that may contact

it) it should be preferably reasonably chemically stable to those fluids so as to maintain its integrity.

Although various types of heat exchangers made simply of ITPs have been described, ITPs sometimes have serious drawbacks when they are the only materials in HESMs. Sometimes an ITP may not be chemically stable to one or more of the fluids in the heat exchanger, for instance, many polyesters hydrolyze or otherwise degrade in the presence of water, water-alcohol, or water-glycol mixtures, especially at higher than ambient temperatures. Many ITPs are relatively permeable to many liquids and/or gases, and therefore allow losses and/or migration of these materials in or from the heat exchanger. Some ITPs may be swollen by one or more of the fluids used in the heat exchanger thereby changing their dimensions and/or physical properties. All of the above are of course problems in plastic heat exchangers.

It has been found that a layer of a thermotropic liquid crystalline polymer (LCP) used in the HESM often alleviates or eliminates one or more of the above mentioned problems. By an LCP is meant a polymer that is anisotropic when tested in the TOT Test described in U.S. Patent 4,118,372. If the LCP layer is placed between a fluid and any particular ITP in the HESM it usually protects that ITP from chemical degradation by the fluid, and/or also often protects the ITP from being swollen by that fluid. In addition, even if the ITP is swollen, the LCP because of its high relative stiffness, and the fact that it is not swollen by many fluids, help the overall HESM maintain its shape and dimensions. Also, the LCP acts as an excellent barrier layer to many fluids. For instance, in automotive heat exchangers which help cool the engine, the commonly used internal coolant is a mixture of a glycol and water, and the external coolant is air. With many ITPs diffusion of water and/or glycol is so rapid that frequent replenishment of the water/glycol mixture is needed. If an LCP layer is included, the diffusion is greatly decreased.

In order to obtain rapid heat transfer through the HESM, thickness through the material between the heat transfer fluids should be as small as possible. This would be true with any material used for an HESM, but is especially important with plastics since their heat transfer coefficients are usually relatively low when compared to metals. Since the LCP is usually the more expensive of the polymers present in the HESM, it is economically preferable to limit its use. Therefore, in most constructions it is preferred that the LCP is present in relatively thin layer(s)

and that layer(s) of the ITP be relatively thick so as to carry much of the structural load of the HESM (i.e., pressure of the fluid(s), maintain structural shape and dimensions, etc.).

5 The HESM is made up of one or more LCP layers and one or more layers of ITP. If more than one layer of LCP or ITP is present, more than one type of LCP or ITP, respectively, can be used. In addition other layers may be present. For example, so called tie layers, also called adhesive layers, may be used to increase the adhesion between various LCP and ITP layers, or between ITP layers
10 or between LCP layers. The number and placement of the various layers in the HESM will vary depending on the particular polymers chosen, the fluids used in or by the heat exchanger, temperature requirements, environmental needs, etc.

 Most commonly, tie layers and LCP layers will be relatively thin
15 compared to the ITP layer(s). Typical constructions are given below, wherein Fluids 1 and 2 represent the fluids involved in the heat transfer:

- (a) Fluid 1/LCP/ITP/Fluid 2
- (b) Fluid 1/ITP-1/LCP/ITP-2/Fluid 2
- 20 (c) Fluid 1/LCP-1/ITP/LCP-2/Fluid 2
- (d) Fluid 1/ITP-1/LCP-1/ITP-2/LCP-2/Fluid 2
- (e) Fluid 1/ITP-1/ITP-2/LCP/Fluid 2
- (f) Fluid 1/LCP-1/ITP-1/ITP-2/LCP-2/Fluid 2

25 In all of the above constructions, tie layers may be present between all, some or none of the various polymer layers.

 Some of the above constructions may be particularly useful in certain situations. If Fluid 1 but not Fluid 2 chemically attacked the ITP, construction (a)
30 may be particularly useful, but (c) and (f) may also be utilized. If both Fluids 1 and 2 attacked the ITP present construction (c) or (f) may be particularly useful. If one wanted to minimize diffusion of one fluid to another, a construction having two LCP layers, such as (c), (d) or (f) could be chosen. If a special surface is required to reduce abrasive damage on the Fluid 1 side, but great stiffness is also
35 required from the ITP, a construction such as (e) could be chosen wherein ITP-1 and ITP-2 have the requisite properties. These and other combinations of layers having the correct properties for various applications will be obvious to the artisan.

Useful LCPs include those described in U.S. Patents 3,991,013, 3,991,014, 4,011,199, 4,048,148, 4,075,262, 4,083,829, 4,118,372, 4,122,070, 4,130,545, 4,153,779, 4,159,365, 4,161,470, 4,169,933, 4,184,996, 4,189,549, 4,219,461, 4,232,143, 4,232,144, 4,245,082, 4,256,624, 4,269,965, 4,272,625, 4,370,466, 4,383,105, 4,447,592, 4,522,974, 4,617,369, 4,664,972, 4,684,712, 4,727,129, 4,727,131, 4,728,714, 4,749,769, 4,762,907, 4,778,927, 4,816,555, 4,849,499, 4,851,496, 4,851,497, 4,857,626, 4,864,013, 4,868,278, 4,882,410, 4,923,947, 4,999,416, 5,015,721, 5,015,722, 5,025,082, 5,086,158, 5,102,935, 5,110,896, and 5,143,956, and European Patent Application 356,226. Useful thermotropic LCPs include polyesters, poly(ester-amides), poly(ester-imides), and polyazomethines. Especially useful are LCPs that are polyesters or poly(ester-amides). It is also preferred in these polyesters or poly(ester-amides) that at least about 50 percent, more preferably at least about 75 percent, of the bonds to ester or amide groups, i.e., the free bonds of $-C(O)O-$ and $-C(O)NR^1-$ wherein R^1 is hydrogen or hydrocarbyl, be to carbon atoms which are part of aromatic rings. Included within the definition herein of an LCP is a blend of 2 or more LCPs or a blend of an LCP with one or more ITPs wherein the LCP is the continuous phase.

Useful ITPs are those that have the requisite properties as described above, and include: polyolefins such as polyethylene and polypropylene; polyesters such as poly(ethylene terephthalate), poly(butylene terephthalate), poly(ethylene 2,6-naphthalate), and a polyester from 2,2-bis(4-hydroxyphenyl)propane and a combination of isophthalic and terephthalic acids; styrenics such as polystyrene and copolymers of styrene with (meth)acrylic esters; acrylonitrile-butadiene-styrene thermoplastics; (meth)acrylic polymers including homo- and copolymers of the parent acids, and/or their esters and/or amides; polyacetals such as polymethylene oxide; fully and partially fluoropolymers such as polytetrafluoroethylene, polychlorotrifluoroethylene, poly(tetrafluoroethylene/hexafluoropropylene) copolymers, poly[tetrafluoroethylene/perfluoro(propyl vinyl ether)] copolymers, poly(vinyl fluoride), poly(vinylidene fluoride), and poly(vinyl fluoride/ethylene) copolymers; ionomers such as an ionomer of an ethylene-acrylic acid copolymer; polycarbonates; poly(amide-imides); poly(ester-carbonates); poly(imide-ethers); polymethylpentene; linear polyolefins such as polypropylene; poly(etherketoneketone); polyimides; poly(phenylene sulfide); polymers of cyclic olefins; poly(vinylidene chloride); polysulfones; poly(ether-sulfones); and polyamides such as nylon-6,6 nylon-6, nylon-6,12, nylon-6,12, nylon 4,6, and the

polyamides from terephthalic acid and/or isophthalic acid and 1,6-hexanediamine and/or 2-methyl-1,5-pentanediamine. Polyamides are preferred ITPs and preferred amides are nylon-6,6, nylon-6, and a copolymer of terephthalic acid with 1,6-hexandiamine and 2-methyl-1,5-pentanediamine wherein 1,6-hexanediamine is about 30 to about 70 mole percent of the total diamine used to prepare the polymer. Especially preferred polyamides are nylon-6,6, nylon-6 and a copolymer of terephthalic acid with 1,6-hexandiamine and 2-methyl-1,5-pentanediamine wherein 1,6-hexanediamine is about 50 mole percent of the total diamine used to prepare the polymer. Included within the definition of ITP herein are blends of 2 or more ITPs or blends of one or more ITPs with an LCP provided that the ITP(s) is the continuous phase.

One or more (if present) of the ITPs may be toughened. Toughening is known in the art, and may be accomplished by adding one or more of a rubber, functionalized rubber, resin which reacts with the ITP such as an epoxy resin, or other materials. Toughened polyamides are preferred.

The polymers may contain other materials conventionally found in polymers, such as fillers, reinforcing agents, antioxidants, antiozonants, dyes, pigments, etc. An especially useful material is a filler with high heat conductivity, which may increase the efficiency of the heat exchanger.

The composition of a tie layer will depend on which two polymers are on either side of it. For instance the tie layer may be an ITP functionalized or grafted to provide adhesion between the ITP and LCP layers, or may be a blend of one or more ITPs and one or more LCPs.

Typical thicknesses for ITP layers will range from about 0.025 to about 0.25 mm. Typical thicknesses for LCP layers will be about 0.01 to about 0.1 mm. Tie layers will usually be as thin as possible, consistent with their providing adhesion between polymer layers. This is usually about 0.01 to about 0.1 mm. The total thickness of the structure is preferably less than about 0.7 mm, more preferably about 0.12 to about 0.5 mm, and especially preferably about 0.15 mm to about 0.4 mm.

Heat exchangers of many different configurations are, made and used, see for instance R. K. Shah, et al., in W. Gerhartz, et al., Ed., Ullmann's Encyclopedia of Industrial Chemistry, 5th Ed., Vol. B-3, VCH Verlagsgesellschaft mbH,

Weinheim, 1988, p. 2-1 to 2-108. As can be seen from this article, and is well known in the art, probably the two most common heat exchange "elements" are the tube and the plate. In a tube type heat exchanger one of the fluids flow through a usually circular cross sectioned tube, while the other fluid flows on the exterior of the tube. Usually many small tubes are employed to create a large heat exchange surface. Sometimes the tubes may be finned for more efficient heat transfer. In a plate element, small passageways, akin to small tubes, are fabricated within a plate of the heat exchange material. One of the fluids flows on the inside of the passageways while the other fluid flows over the exterior surface of the plates. The passageways are usually small to increase surface area, and multiple plates are often used. All of the discussion about heat exchange surface materials also applies to heat exchange panels.

For tube type heat exchangers, the multilayer material described herein can be made by multilayer coextrusion of a tube, see for instance U.S. Patent 5,288,529. However, LCPs when so extruded tend to be weak in the transverse direction (perpendicular to the long axis of the tube). Such problems can be solved by using a counterrotating die for the LCP portion of the extruded tube, as described in U.S. Patents 4,963,428 and 4,966,807, and G.W. Farell, et al., Journal of Polymer Engineering, vol. 6, p. 263-289 (1986). The tubes can be assembled into a full heat exchanger by inserting them into tanks with proper size holes and sealing the holes with a filler such as epoxy resin, or by heat sealing.

Heat exchanger plates of the layered material described herein may be made by relatively standard methods. They may be directly coextruded, complete with passages in them. A flat sheet or film may be coextruded, thermoformed into the correct shape and joined adhesively or by heat into the plate. Such coextrusions are known processes, see for instance H. Mar, et al., Ed., Encyclopedia of Polymer Science and Engineering, 2nd Ed., Vol. 6, John Wiley & Sons, New York, 1986, p. 608-613, *ibid.*, Vol. 7, 1987, p. 106-127, all of which is hereby included by reference. Individual films or sheets of the ITP(s) and LCP(s) may be laminated together, then formed into a heat exchanger plate. For fabrication of a plastic heat exchanger made with plates see U.S. Patent 4,955,435.

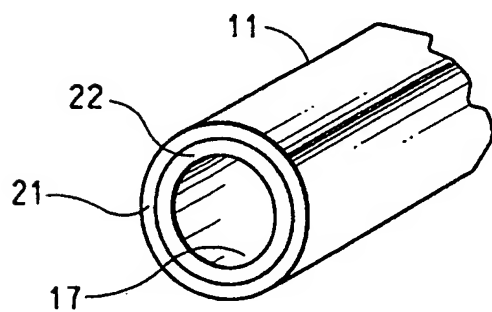
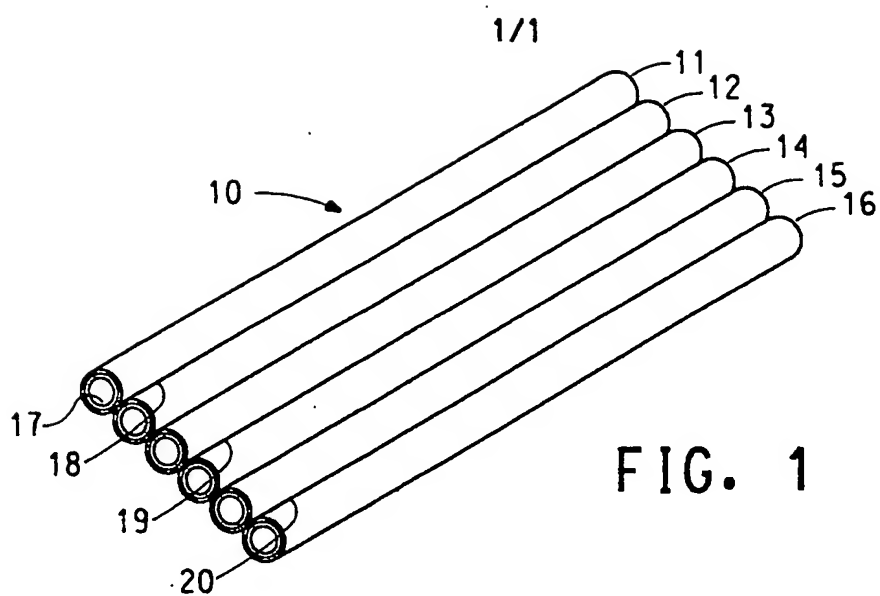
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The heat exchangers described herein are useful for automotive and other vehicle uses, in aircraft, as comfort heat exchangers, and various ventilating, heating and air conditioning applications. They are particularly useful as liquid-

gas heat exchangers used to cool automotive gasoline or diesel engines. In that case the liquid is water, water and a glycol, or water and an alcohol.

CLAIMS

1. A heat exchanger made from polymeric tubes in the form of tube sheets with a multiplicity of at least three tubes adjacent each other in a plane, bonded together by an outer layer on the tubes which is melted together.
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2. The heat exchanger of claim 1 wherein the tubes are made of polyamide.
- 10 3. The heat exchanger of claim 1 wherein at least five tubes are held adjacent each other in a plane.
4. A tube sheet for use in a heat exchanger of claim 1 wherein at five tubes are held adjacent each other by a melted layer at the surface of the tubes.
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5. A method for making a tube sheet of claim 4 wherein a multiplicity of tubes is provided with a lower-melting polymer on the outside surface of each tube, and wherein the tubes are arranged in a plane adjacent each other and then heated so that the outer surfaces melt together to adhere the tubes to each other.
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INTERNATIONAL SEARCH REPORT

Inter. Application No

PCT/CA 00/00742

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 F28D7/00 F28F21/06 B29C65/02

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 F28F B29C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category * | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|------------|---|-----------------------|
| P,X | FR 2 785 375 A (VALEO THERMIQUE MOTEUR) 5 May 2000 (2000-05-05) page 5, line 36 -page 6, line 31; figure 3 --- | 1-5 |
| Y | EP 0 168 558 A (AKZO GMBH) 22 January 1986 (1986-01-22) page 6 page 8, paragraph 2 - paragraph 3; figures 16,21 --- | 1-5 |
| Y | WO 98 55815 A (DOSHI SHAILESH ;FARKAS NICHOLAS (CA); STEVENS KENNETH EARL (CA)) 10 December 1998 (1998-12-10) claim 1; figure 1 --- | 1-5 |
| A | US 4 935 462 A (CESARINO ANTHONY J) 19 June 1990 (1990-06-19) column 3, line 29 - line 63 --- | 1-5 |

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☒ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

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Date of the actual completion of the international search

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

| Category * | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|------------|---|-----------------------|
| A | US 5 195 240 A (SHUSTER JERRY P ET AL) 23 March 1993 (1993-03-23) cited in the application claim 1; figures ---- | 1-5 |
| A | DE 195 29 227 A (STEAG AG) 13 February 1997 (1997-02-13) column 2, line 7 - line 11 column 3, line 11 - line 16; claims 1,2; figure 1 ---- | 1-3 |
| A | US 3 438 432 A (WETCH JOSEPH R ET AL) 15 April 1969 (1969-04-15) column 3, line 70 -column 4, line 8; figures 3,4 ----- | 1-3 |

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/CA 00/00742

| Patent document cited in search report | Publication date | Patent family member(s) | Publication date |
|---|---------------------|--|--|
| FR 2785375 A | 05-05-2000 | NONE | |
| EP 0168558 A | 22-01-1986 | DE 3426445 A DE 3575695 D JP 1814016 C JP 5023932 B JP 61043528 A US 4740344 A | 30-01-1986 08-03-1990 18-01-1994 06-04-1993 03-03-1986 26-04-1988 |
| WO 9855815 A | 10-12-1998 | EP 0988500 A | 29-03-2000 |
| US 4935462 A | 19-06-1990 | CA 1327415 A DE 3882069 A DE 3882069 T EP 0287271 A US 5039370 A | 01-03-1994 05-08-1993 16-12-1993 19-10-1988 13-08-1991 |
| US 5195240 A | 23-03-1993 | AU 608148 B AU 3279589 A CA 1329472 A DE 68913222 D DE 68913222 T EP 0337802 A JP 2022041 A JP 2966427 B KR 177796 B | 21-03-1991 19-10-1989 17-05-1994 31-03-1994 04-08-1994 18-10-1989 24-01-1990 25-10-1999 15-04-1999 |
| DE 19529227 A | 13-02-1997 | AT 186775 T DE 59603681 D WO 9706397 A EP 0843804 A | 15-12-1999 23-12-1999 20-02-1997 27-05-1998 |
| US 3438432 A | 15-04-1969 | BE 717094 A DE 1751590 A FR 1571767 A GB 1240141 A IL 30252 A NL 6808746 A SE 338059 B | 02-12-1968 08-07-1971 20-06-1969 21-07-1971 30-08-1972 27-12-1968 30-08-1971 |